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Preparation of Nitrogen-Doped Few-Wall Carbon Nanotubes for Facile and Sensitive Determination of Dopamine

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Nitrogen-doped carbonaceous materials have attracted tremendous attention because of their high activity in electrocatalysis. In this paper, nitrogen-doped few-wall carbon nanotube (NFWNT) with 3-5 walls was successfully synthesized via thermal annealing employing carbon nanotube (CNT) and urea as raw materials by solvothermal method. The morphology and microstructure of NFWNT was characterized by Transmission electron microscope (TEM), X-ray powder diffractometer (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. NFWNT possessed excellent electrocatalytic activity towards the electrocatalytic oxidation of dopamine (DA) due to its unique molecular structure and properties. The sensitive detection platform based on NFWNT modified electrode (NFWNT@GCE) was constructed. Furthermore, a low detection limit of 0.26 μM (S/N=3) with the wide linear range of 1μM to 500μM and fast response (within 3 s) are obtained. This new discovery provides a simple and useful platform for detecting biomolecules and other electrochemical sensing applications.

Keywords: Determination; Dopamine; Nitrogen-doped few-wall carbon nanotubes (N-FWNT); Glassy carbon electrode (GCE)

1. INTRODUCTION

Dopamine (DA) is one of the most important neuron transmitter compounds widely existed in the brain for message transfer in the central nervous system of mammals [1, 2], which plays a pivotal role in the function of human metabolism, cardiovascular, renal, central nervous and hormonal systems.[3,4] Abnormal DA concentration may lead to a disease called Parkinson's disease in which a person loses the ability to perform a smooth and controlled action. [5,6] DA can be supplied as a medication, however, its excess dosage may act on the sympathetic nervous system causing increased heart rate and blood pressure. Therefore, it is of great significance to develop simple and rapid

determination methods of DA. Electrochemical technique is usually used for the detection the DA in different solution, such as, sensitivity, selectivity simplicity and rapid response time. [7, 8] Due to highly electrochemical activity of dopamine, DA determination is always attracting the tremendous interest in electroanalysis. Some methods based on the modification of traditional electrode materials have been reported for the determination of DA, such as: polychromotrope 2B modified glassy carbon electrode(GCE) [9], Nafion/carbon-coated iron nanoparticles-chitosan composite film modified electrode [10], PtAu hybrid film modified electrode [11], copper nanoparticles-multiwalled carbon nanotubes/GCE (Cu-MWCNT/GCE) [12] , and nitrogen doped graphene (NG) /GCE[13].

Due to their excellent electrical, mechanical, thermal, and optical properties, carbon nanotubes (CNTs) have shown great potential use in various applications, such as electrodes, actuators, filters, ultrafast photonics, structural fibers. [14] Especially, CNTs can promote the electron transfer between electroactive substances and electrodes and have excellent electrocatalytic properties for different molecules and biomolecules [15, 16]. Therefore, they have been extensively used in many research fields since they were discovered in 1991.

Chemical doping with heteroatoms such as nitrogen or boron atoms is an effective strategy to modulate electronic properties and surface chemistry for carbon materials [17]. For instance, the nitrogen doped carbon structure can be easily through the formation of C-N bond due to the similarity of the atomic size and valence electron structure. To date, nitrogen doped CNTs (N-CNTs) have been successfully prepared by CVD in the presence of nitrogen containing species (i.e., NH_3 and pyridine), and by the thermal decomposition of macrocycles containing nitrogen atoms [18, 19]. The resultant N-CNTs show much higher sensitivity in biosensing applications and excellent electrocatalytic activity towards oxygen reduction reaction (ORR) [20, 21]

In this work, we directly synthesize nitrogen-doped few-wall carbon nanotubes (NFWNTs) by one-step solvothemal method and use a simple and rapid method to fabricate the glassy carbon modified electrode with as-prepared NFWNTs. The microstructure of NFWNTs is characterized in detail. Moreover, cyclic voltammetric techniques have been used to estimate the electrochemical behavior of DA on the modified glassy carbon modified electrode with NFWNTs. The results indicate that NFWNTs modified electrode show an excellent electrocatalytic activity to oxidize small biological molecules. Therefore, we believe that the one-step method of preparation functional nanomaterials will have a large application in the future.

2. EXPERIMENTAL

2.1. Raw materials

Few-walled carbon nanotubes (FWNTs) with the lengths of 0.1-10 μm were purchased from Chengdu Organic Chemicals Co., LTD. Chengdu, China). Urea, dopamine and ethylene glycol were obtained from Sinopharm Chemical Reagent CO. Ltd (China), All chemicals were of analytical grade and solutions were prepared with ultrapure water (>18MΩ).

2.2 Preparation of NFWNTs

In a typical experiment, an appropriate amount of FWNTs (1.0 g) and ethylene glycol (75ml) was added to a 100 ml capacity of the stainless steel autoclave, and mixed into a homogeneous aqueous glucose solution. The reaction furnace was kept for 24 hours at 180 °C , and then cooled to room temperature naturally. A dark precipitate was collected and washed with absolute ethanol three times. The as-made **NFWNTs** were then dried in a vacuum at 60 °C for 10 h.

2.3. Preparation of NFWNT modified glass carbon electrode (N-FWNT @GCE)

Prior to modification, the glassy carbon electrode (GCE, φ=3mm) was pretreated to mirror-like as the procedures [22]. The cleaned GCE was dried with blowing N_2 gas before modifications. The electrochemical tests were carried out with a CHI 842 station. Pt wire and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The NFWNT -modified GCE was prepared by dropping the NFWNT suspension (10μL, 1mg/mL) onto the pretreated bare GCE and dried in air. The NFWNT -modified GCE (NFWNT@GCE) was directly used for the detection of DA.

2.4. Characterization

The morphology of NFWNT was characterized using a Hitachi-2100 TEM at a 200 kV accelerating voltage and The TEM samples were prepared by drying a droplet of the **NFWNT**s suspensions on a Cu grid. X-ray photo-electron spectroscopy (XPS, Kα) analyses were carried out using a Thermo Fisher X-ray photoelectron spectrometer equipped with Al radiation as the probe, with a chamber pressure of 5×10^{-9} Torr. The power was 72 W, and the pass energies were 200 eV and 50 eV for survey scans and high-resolution scans, respectively. Electrochemical measurements were carried out at a standard three-electrode cell on a CHI 842 electrochemical station (CH Instrument, USA) with a modified GCE as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference.

3. RESULTS AND DISCUSSION

3.1 Preparation and characterization of NFWNT

The TEM image of the as-prepared NFWNTs is shown in Fig. 1A. A lot of clean carbon nanotube, with a perfect tube morphology, can be clearly observed. The NFWNTs exhibit uniform diameter. Fig. 1B shows the number of walls is 5 and the diameter about 5nm. The morphology the excellent dispersing ability of NFWNTs should be beneficial to improve the specific surface area of electrodes. The high specific surface area of electrodes will have more available active sites for DA.

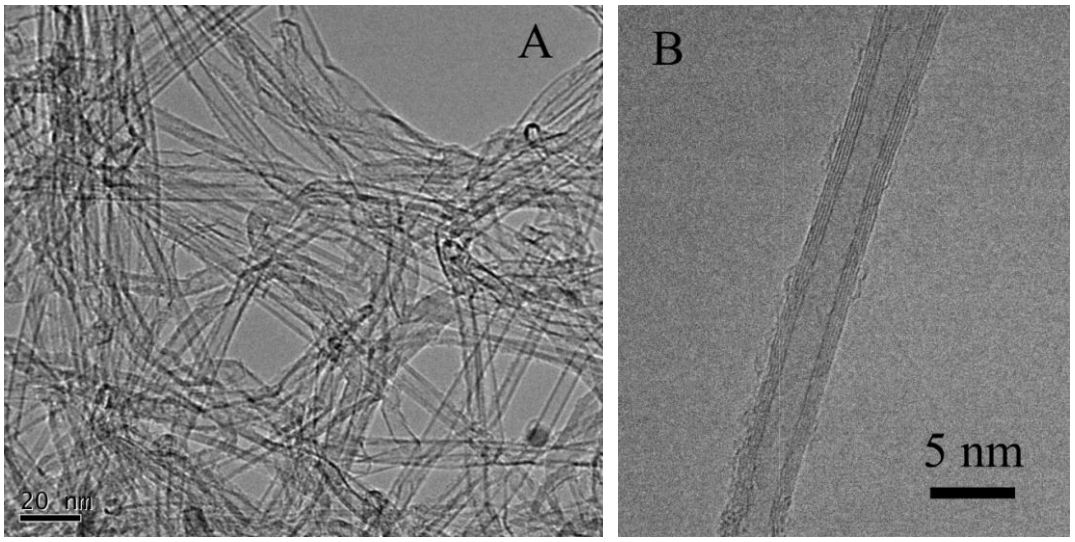

Figure 1. TEM images of as-prepared NFWNTs

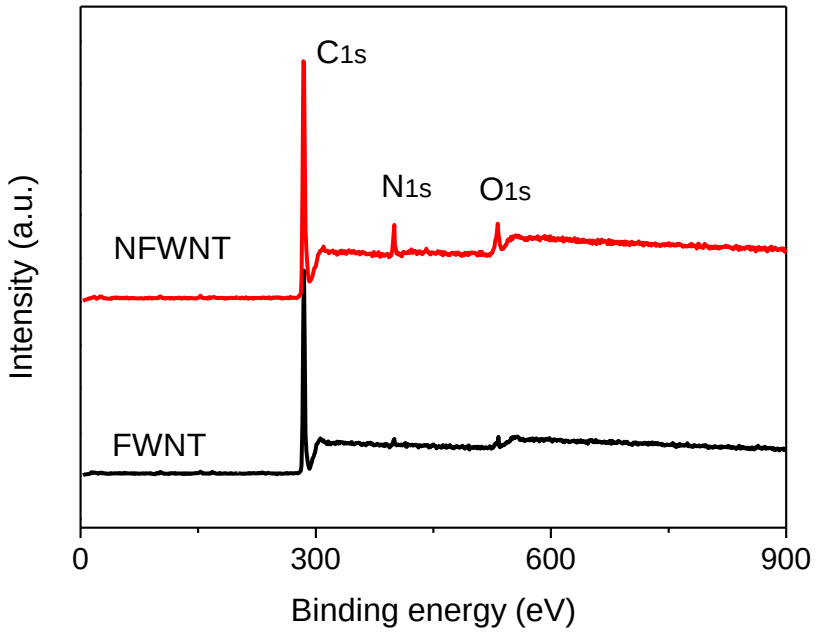

Figure 2. XPS spectra of FWNT and NFWNTs

Table 1 Atomic concentrations in FWNT and NFWNT from XPS

Sample	C%	O%	N%
FWNT	99.53	0.27	0.20
NFWNT	87.30	5.61	7.09

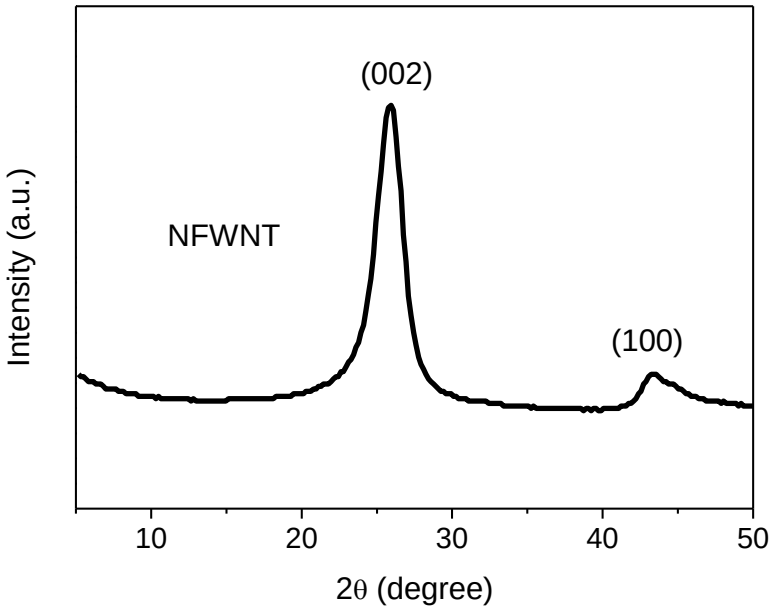

Figure 3. XRD patterns of the NFWNTs.

XPS was performed to confirm the chemical composition and changes in the FWNT and NFWNT. It indicates that the existence of the main C1s (284.5eV), O1s (532eV), and N1s (399.7eV) peaks clearly as shown in Figure 3. XPS of NFWNT shows a new small peak of nitrogen, indicating N atoms have been successfully incorporated into carbon frameworks in NFWNT. It is worth noting that XPS can not detect the hydrogen atom. Table1 shows atomic concentrations from XPS. The elemental content analysis from the XPS data reveals the mass composition of NFWNT: C 87.3 %, N 7.09%, O 5.61%.

The as-obtained NFWNT is also characterized by XRD. As shown in Figure 3, the typical (002) and (100) peaks of NFWNTs are obtained at 2θ of 25.9◦ and 43.3◦, respectively, which is in consistent with the previous results.

3.2 Influence of solution pH

The effect of pH value on the current and peak potential responses of 0.5 mM dopamine at NFWNT@GCE was investigated by changing pH value from 4.5 to 7.5 in 0.1 M PBS. The oxidation peak potential shifts to the negative value with the increase of pH value as shown in Figure 4A. It indicates that the proton is involved in the electrode surface reaction. Furthermore, it was also found that the oxidation peak exhibited highest current when the pH value was 7.0 as shown in Figure 4B. Therefore, pH 7.0 was set for further experiment.

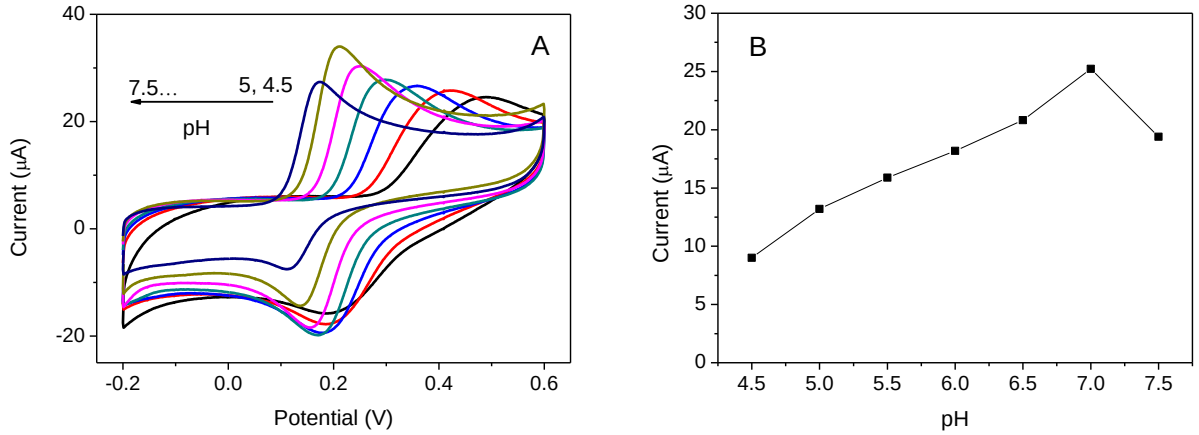

Figure 4. The effect of buffer pH on the peak current of dopamine. Buffer: 0.1 mol/ L PBS. pH: 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5.

3.4 Influence of scan rate

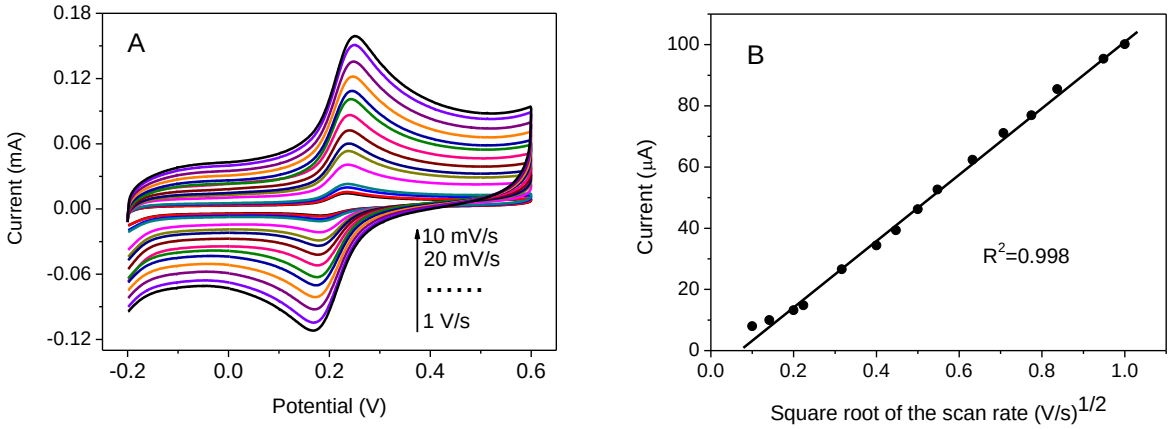

Figure 5. (A) Cyclic voltammograms of 0.5mM DA with different scan rates (*v*) at NFWNT@GCE in 0.1mol/L PBS (pH=7) (from the inner to the outer are 10, 20,……1000 mV/s, respectively). (B) The relationship between oxidation peak currents and scan rates.

To further investigate the electrochemical oxidation mechanism of dopamine at the NFWNT@GCE, the influence of scan rate (*v*) on the current response of dopamine was studied in detail. As shown in Figure 5, along with the increase of the scan rate, the redox peak currents increased simultaneously, accompanied with an enlargement of the peak separation. The peak current response of the NFWNT@GCE exhibits a good linear dependence with correlation coefficient of 0.998. This behavior illustrates that the redox of DA on the modified GCE is predominantly diffusion controlled process.

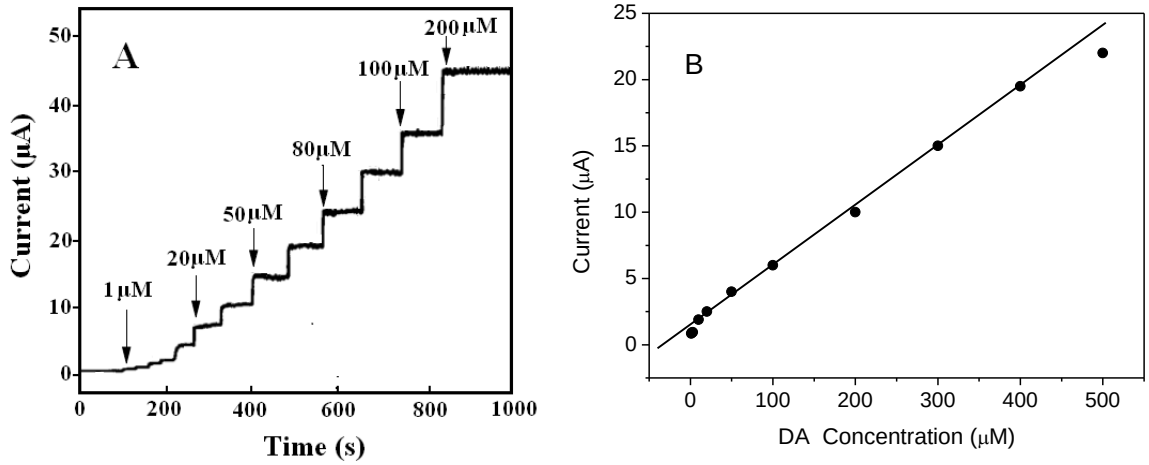

Figure 6. (A) Current–time responses at +0.30V with a successive addition of DA solution for the NFWNT modified GC electrode respectively. (B) The dependence of the current response vs. DA concentration at NFWNT@GC electrode.

Figure 6A shows that the relationship between the DA concentration and current response is studied. The amperometric responses increased as a function of the DA concentration at optimal potential of 0.3V in 0.1mol/L PBS (pH=7). It is observed that a significant enhancement of current responses was obtained and the steady-state current was achieved less than 3 seconds after each addition of DA solution, which suggests a fast and sensitive response to DA. The result indicates that the as-prepared NFWNTs exhibit very sensitive and rapid response characteristics, which is attributed to the highly electroconductivity and large active surface area of as-prepared NFWNTs. The current response and the linear range are found to be 1–500 μM with a correlation coefficient of 0.986 as shown in Figure 6B. The limit of detection (LOD) was estimated to be 0.26 μM (at signal/noise = 3). There are two main reasons for this excellent electrochemical activity of NFWNTs. Firstly, NFWNT has a large active surface area, excellent conductivity and a large number of edge-plane-like defective sites, which accelerate electron-transfer between the electrode and species in solution and facilitate high catalytic activity towards DA. Moreover, with the N atoms doping in FWNTs, structural deformation was formed because of the local tension emerging in the hexagonal carbon network [23], which can enhance the electron transfer and chemical reaction activity [24] in means of the additional lone electron pair of N atoms providing negative charge to the delocalized π system in sp2 hybridized carbon skeleton. Based on the higher electrocatalytic activities to the DA, NFWNT may be a good carbonaceous material for constructing a new and promising electrochemical sensing platform for detecting other biomolecules.

Besides, the literature comparison of these results to the detection of dopamine by using different modified electrodes is shown in Table 2. It can be seen that DA detection on the NFWNTs@GCE could achieve wider linear range and lower detection limit. These data further indicated that NFWNTs exhibit a significant improvement of electrochemical performance towards DA.

Table 2. Comparison of other modified electrodes for DA detection.

Modified electrode	Linear range (μM)	LOD (μM)	References
NCF/GCE	1.0–200	0.5	[25]
Pd/CNFs/CPE	0.5–160	0.2	[26]
CNTs-ionic liquid gel/GCE	1–10	0.1	[27]
SDS-MWCNTs/GCE	20–200	3.75	[28]
MWCNT/GCE	3-200	0.8	[29]
Graphene/GCE	4-100	2.64	[30]
PLA/GCE	0.8–500	0.3	[31]
AgNP/CNTPE	0.8–64	0.3	[32]
MWCNT/Au electrode	0.5–400	0.2	[33]
NFWNT	1-500	0.26	This work

ABBREVIATIONS:
NCF: Nitrogen-doped carbon nanofiber, CPE: carbon paste electrode, SDS: sodium dodecyl sulphate, PLA: poly(L-arginine), AgNP: Silver nanoparticles, CNTPE: carbon nanotube paste electrode;

4. CONCLUSION

In summary, NFWNT with 3-5 walls was prepared through a simple and efficient solvothermal approach. Under the optimized conditions, the as-prepared NFWNT exhibited a high degree of electrocatalytic activity towards the oxidation of biomolecules such as dopamine (DA) due to its unique structure and properties originating from nitrogen doping. The sensitive detection platform based on NFWNT modified electrode (NFWNT@GCE) was constructed. Furthermore, a low detection limit of 0.26 μM (S/N=3) with the wide linear range of 1μM to 500μM and fast response (within 3 s) are obtained. We believe that such a facile and effective assembly method will provide a new way for electrochemical sensing and other electrocatalytic applications.

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